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SUMMARY REPORT
STUDIES OF INTERFACIAL SURFACE ENERGIES

by

George A. Lyerly and Henry Peper

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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HARRIS RESEARCH LABORATORIES, INC.
6220 Kansas Avenue, N. E.
Washington, D. C. 20011

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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Fluid Dynamics Section
Donald Petrash

HARRIS RESEARCH LABORATORIES, INC.
6220 Kansas Avenue, N. E.
Washington, D. C. 20011

STUDIES OF INTERFACIAL SURFACE ENERGIES

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ABSTRACT

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The densities and surface tensions at 20°C. of water, absolute ethanol, uns-dimethyl hydrazine (UDMH), hydrazine, Arizine-50, nitric acid propellant IIIB, di-nitrogen tetroxide, and 90% hydrogen peroxide were determined by the Westphal and the duNouy methods respectively. The contact angles of each of these liquids on glass and on prepared surfaces of aluminum alloy, titanium alloy, and stainless steel were observed using the sessile drop method. Each of the liquids wet each of the solids initially. Changes in the contact angle due to surface aging were observed, and differences in the liquid spreading effects were noted.

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SUMMARY

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As a part of the overall study of the behavior of rocket engine propellants stored in space vehicle tanks while exposed to weightlessness, the contact angles of liquid propellants on prepared surfaces of tank materials were experimentally determined. The surface tensions and densities of the liquid propellants were determined to complement the contact angle measurements.

Initial low contact angles in the range of 2^{o} - 0^{o} accompanied by spontaneous spreading were observed for drops of each liquid on each solid substrate. Aging experiments showed that most of the liquid-solid systems observed remained wet. The exceptions were the liquid solid pairs of conductivity water on polished aluminum and stainless steel surfaces and of 90% hydrogen peroxide on polished aluminum surfaces.

The Marangoni or "wineglass" effect was observed to occur in the spreading of uns-dimethyl hydrazine (UDMH), Arizine-50, and di-nitrogen tetroxide on each solid surface. This effect was observed also for 90% hydrogen peroxide on satinized stainless steel. Over the time period that the Marangoni effect was observed, the liquids wet the solid surfaces with a true zero contact angle.

Author

INTRODUCTION

The NASA Lewis Research Center is currently conducting a study of the problems associated with the behavior of rocket engine propellants stored in space vehicle tanks while exposed to weightlessness (zero gravity) during coasting periods. A knowledge of the contact angles of liquid rocket propellants on tank materials will be needed to design suitable propellant tank configurations to control the positioning of the liquid and vapor within the tank.

The purpose of this investigation was to experimentally determine the solid-liquid interfacial contact angle of each of eight liquids on each of seven solid surfaces. The densities and surface tensions of the liquids were determined to complement the contact angle measurements. The liquids and solids used in this study were as follows: liquids - water, alcohol, 90% hydrogen peroxide, hydrazine, uns-dimethyl hydrazine (UDMH), Arizine 50, nitric acid propellant type IIIB, and di-nitrogen tetroxide; solids - glass, aluminum, stainless steel, and titanium alloy. The metals were given both a polished and a randomly roughened finish. The complete liquid and solid specifications are listed in the Experimental Section.

Although isolated measurements of the densities and surface tensions at various temperatures of some of the fuels and oxidizers were found in the literature, no tabulation of these measurements at one temperature was found. The present work provides a systematic tabulation of the surface tensions and densities of the liquid propellants at one temperature (20°C.) and records the observed contact angles of these liquids at the same temperature on clean specimens of tank materials and on glass.

The behavior of liquids in weightlessness has been studied experimentally in a series of papers by Petrash et al (1, 2, 3): initially, in a free-fall drop tower as a function of tank geometry, liquid filling, and liquid wetting properties; and then in the flight of the MA-7 spacecraft in a spherical tank containing a cylindrical capillary tube (4). These experiments demonstrate the practical effectiveness of using liquid-solid capillary forces to control the positioning of a liquid in a tank under zero gravity conditions. The results presented in this report provide part of the numerical data necessary to design capillary spaces to control the positioning of the currently used liquid propellants.

Valuable assistance was received from Mr. DeWitt C. Knowles of Harris Research Laboratories for the design of the experimental apparatus and from Dr. Anthony M. Schwartz of Harris Research Laboratories in interpreting the observations of liquid spreading effects.

EXPERIMENTAL

Since the purpose of this work was to obtain accurate data, considerable attention was paid to the experimental procedures used for determining the contact angles, surface tensions, and densities; for cleaning the solid surfaces, glassware, and metalware; and for polishing and satinizing the metal specimens. The propellants and metal alloys used for this work were obtained from NASA suppliers under the appropriate Military Specification or ASTM Specification. The methods of Zisman and co-workers (5) were used for many of the procedural details of the contact angle measurements. The measurements made with toxic fuels or highly reactive oxidizers were done in a laboratory hood. Figure 1 is a photo of the apparatus used for contact angle measurements with di-nitrogen tetroxide. The thermostat is at the left of the hood bench; the contact angle goniometer is in the center, and the delivery system for the di-nitrogen tetroxide is at the right. The surface tensions and densities were determined by replacing the contact angle goniometer with the appropriate instrument.

A. Materials

1. Material Specifications

Liquids

1. Water -- Pyrogen free, inorganic contamination less than 0.5 pts/million, resistance no less than 0.6 megohms/cc at 20°C.

2. Ethanol -- Chemically pure, undenatured, anhydrous ethanol (200 proof).

3. Hydrazine (N_2H_4) -- Military specification, MIL-P-2653A (USAF), 31 July 1959.

4. UDMH (uns-dimethyl hydrazine) -- Military specification MIL-D-25604B, 12 September 1958 and MIL-D-25604B Amendment 1, 5 March 1959.

5. Arizine 50 -- 0.5/0.5 parts by weight hydrazine and UDMH.

6. 90% hydrogen peroxide -- Military specification MIL-H-16005C, 10 September 1956.

7. Nitric acid propellant type IIIB -- Military specification MIL-P-7254E, 8 September 1959 and MIL-P-7254E Amendment 1, 17 August 1961.

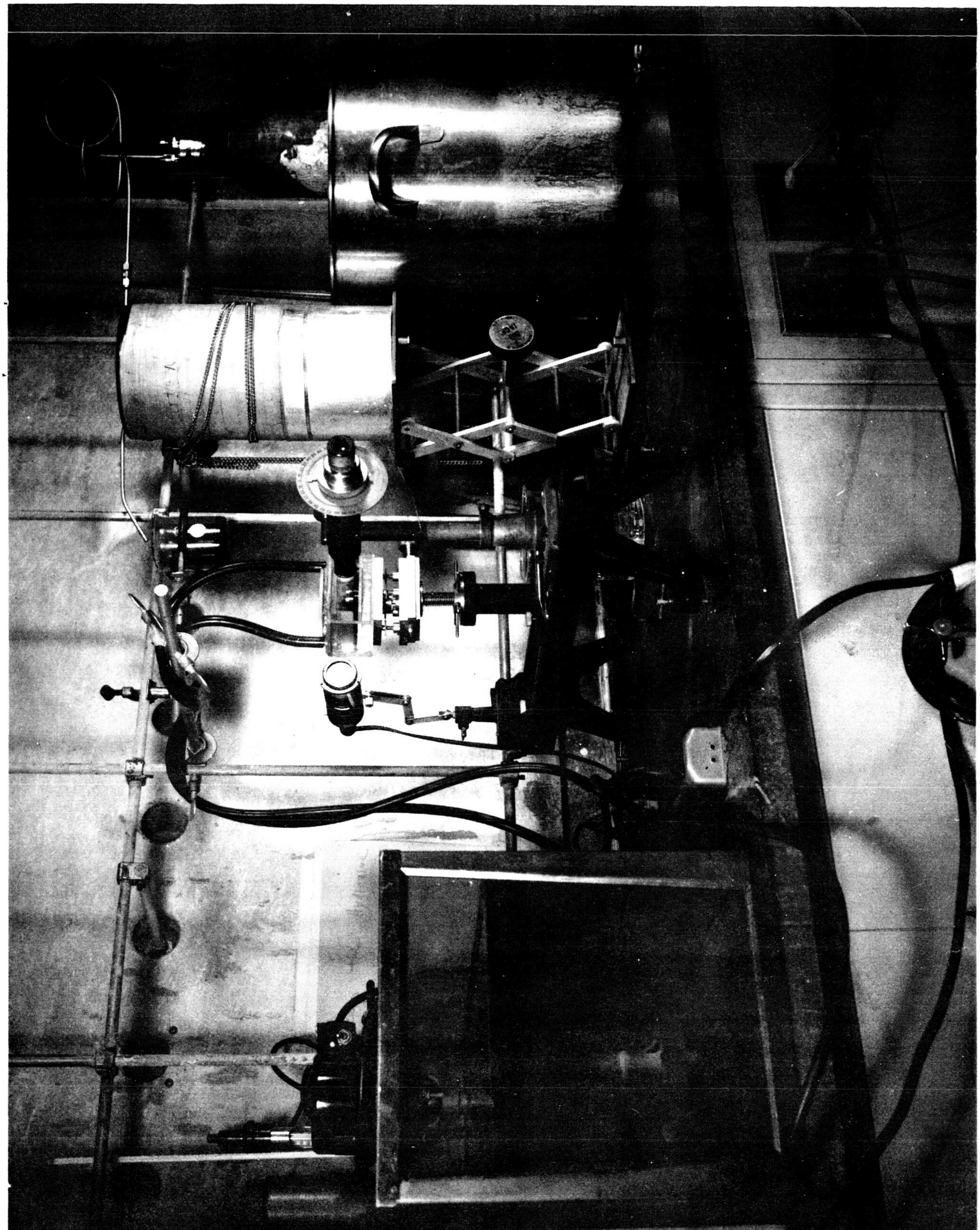


Figure 1

Equipment for Measuring Contact Angles with Di-Nitrogen Tetroxide

8. di-Nitrogen tetroxide (N_2O_4) -- Military Specification MIL-P-26539A, 31 July 1961, and MIL-P-26539A Amendment 1, 5 April 1963.

Solids

1. Glass -- Corning "Pyrex" Brand Chemical Glass No. 7740.

2. Type 301 Stainless steel -- A1S1, Fed. Std. 66B, Fed. Spec. QQ763C.

3. Type 6961 T6 Aluminum -- Fed. Spec. QQ-A-00200/8 or ASTM B221-64.

4. Titanium alloy, Grade 6 -- ASTM B348-59T, Mil. Spec. MIL-S-5059A.

2. Solid Specimens

Six types of prepared metal specimens and one type of plate finished Pyrex 7740 chemical glass were used for the solid surfaces. Some specimens of each metal listed were given a polished specular finish, and others were given a satin finish. Plate finished 1" x 1" squares of Pyrex type 7740 chemical glass were used as received.

Metal specimens -- Cylindrical planchets, 1" diameter x 318" height, were cut from 1" round bar stock of type 6061 T6 aluminum alloy and of grade 6 titanium alloy ASTM B348-59T. The planchets cut from type 301 stainless steel were 1/8" in height since this material was received in sheet form. The two faces of each planchet were ground parallel using a Norton traveling bed surface grinding machine. Six planchets were prepared from each alloy.

3. Metal Specimen Finishing (6)

Fine grinding and pre-polishing -- After the planchet faces were surface ground, fine grinding was done by hand under water on a Lunn-Labor wet grinding table beginning with number 220 grit silicon-carbide paper and finishing with number 600 grit silicon-carbide paper. Pre-polishing was done on a Fisher polishing wheel using Buehler No. 1 AB Polishing Alumina (aqueous slurry) on a Buehler AB silk Polishing Cloth followed by a finer polish using Buehler AB Gamma No. 3 Polishing Alumina (aqueous slurry) on a fresh AB Silk Cloth.

Fine polishing -- Planchet fine finishing was done on the Fisher Polishing wheel using an aqueous slurry of Buehler Magomet on a Buehler Micropore cloth for the aluminum planchets and Buehler AB Gamma No. 3 Polishing Alumina on a Buehler Micropore cloth for the titanium and stainless planchets.

Satinizing -- Fine polished planchets were satinized by a sandblasting technique using 80-120 mesh silica blown by oil free nitrogen. The sandblasting apparatus consisted of an Erlenmyer suction filter flask (500 ml) containing the silica and fitted with a rubber stopper through which a loose fitting 30 cm. length of 10 mm. glass tubing was positioned so that its bottom touched the silica. The regulator gauge was set at 10 psig. The powdered silica was impinged against the planchet from a distance of six inches until uniform roughening had been obtained.

B. Procedures

1. Contact Angle Measurements

The following operational sequence was used for each contact angle measurement: 1) cleaning and filling the contact angle cell; 2) cleaning and inserting the capillary transfer pipette; 3) cleaning and inserting the solid specimen; and 4) making the measurement. Two types of contact angle experiments were done. In the first type of experiment, six initial advancing and receding contact angles were obtained for the test liquid on the clean, dry solid surface. In the second type of experiment advancing and receding contact angles were measured on a continuously aging surface after the initial drop was placed on the clean, dry solid surface. The following paragraphs describe these two types of experiments.

Measurement of advancing and receding contact angles on freshly cleaned solids -- Contact angles were measured by the sessile drop method in which a drop of the test liquid was placed on a plane, horizontal solid specimen and the contact angle at the intersection of the liquid-vapor-solid interface was measured using a telescope having a goniometer eyepiece (7). The solid specimen was placed in a covered, water jacketed, rectangular optical cell. A layer of the test liquid 1/8" deep was placed in the bottom of the optical cell to insure rapid vapor saturation of the cell atmosphere. A capillary pipette was inserted into the cell interior through a 1/16" hole in the glass cover plate to transfer liquid within the cell.

In a typical measurement, the clean optical cell (see Optical Cell Cleaning) containing the test liquid was placed on the goniometer platform and connected to the Haake circulator. A clean capillary pipette was then placed through the cell cover plate. After a 30 minute equilibration time, a solid specimen was cleaned and dried (see

Specimen Cleaning); the cell cover plate was moved aside momentarily; the solid specimen was placed on the bottom of the optical cell and the cover plate was replaced. A sample of liquid was then withdrawn from the bottom of the cell into the capillary pipette and a drop 1 mm. in diameter was allowed to fall free onto the solid surface to produce an advancing contact angle. The contact angles of both the right-hand and left-hand edges of the drop were recorded. Receding angles were generated by withdrawing an increment of liquid from the top of the drop, and the right-hand and left-hand angles were recorded as before. If the liquid continued to spread, as with absolute ethanol, the planchet was removed from the test cell, recleaned, dried, and the measurement was repeated on two more drops on different areas of the same solid specimen. The measurement sequence was repeated for a second solid specimen of the same type. The corresponding advancing and receding contact angles from six different drops were averaged together to give the values reported in Table I.

The contact angle goniometer contained identical optics and the same translational motions as Zisman's instrument. The contact angle goniometer scale was divided into 1° intervals. The contact angle data were recorded to the nearest whole degree. The variation in the observed angles was less than a half-degree. The estimated variation in contact angles was noted but was not measured since the total variation was less than the instrument resolution.

Measurement of advancing and receding contact angles on an aging surface -- The second type of experiment was a time study in which a single drop of liquid was placed on a cleaned dry planchet; the advancing angles were observed; an increment was withdrawn; the receding angles were observed; a five minute wait was taken; an increment was added to the drop; advancing angles were read again, and the sequence was repeated at five minute intervals for a thirty minute time period. It should be emphasized that these angles were not averages but were single observations made sequentially.

The appearance of a drop forming a finite contact angle as viewed from above and through the goniometer telescope is illustrated in the photographs in Figures 2 and 3.

2. Surface Tension Measurements

The surface tensions of the liquid propellants used in this study, except 90% hydrogen peroxide, were measured using the platinum ring and Cenco du Nouy tensiometer (8). The Harkins and Jordan (9,10) corrections for the weight of liquid raised by the ring during a measurement were used. The surface tension of the 90% hydrogen peroxide was measured using a Pyrex glass Wilhelmy plate and an analytical balance (11). It was necessary to use the glass Wilhelmy plate for the

TABLE I

CONTACT ANGLES OF LIQUID PROPELLANTS AND WATER AGAINST HIGH ENERGY SURFACES

Type of Surface:	Pyrex Glass		Type 6061 T6 Aluminum				ASTM B348-59T Grade 6 Titanium Alloy				Type 301 Stainless Steel			
			Polished		Satinized		Polished		Satinized		Polished		Satinized	
Liquid	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.
Water	2°	1°	2°	2°	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°
Hydrogen peroxide: 90%	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°
Absolute ethanol	1°	0°	1°	0°	1°	0°	2°	1°	2°	1°	2°	1°	2°	1°
di-Nitrogen tetroxide	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°
Fuming nitric acid Type IIIB	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°	0°
Hydrazine	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°	0°	0°	2°	1°
UDMH (uns-dimethyl hydrazine	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°
Arizine 50 - (0.5/0.5) N_2H_4/UDMH	2°	1°	2°	1°	2°	1°	2°	1°	2°	1°	0°	0°	0°	0°

Figure 2

A drop of 90% Hydrogen Peroxide Viewed From Above Maintaining a Finite Contact Angle

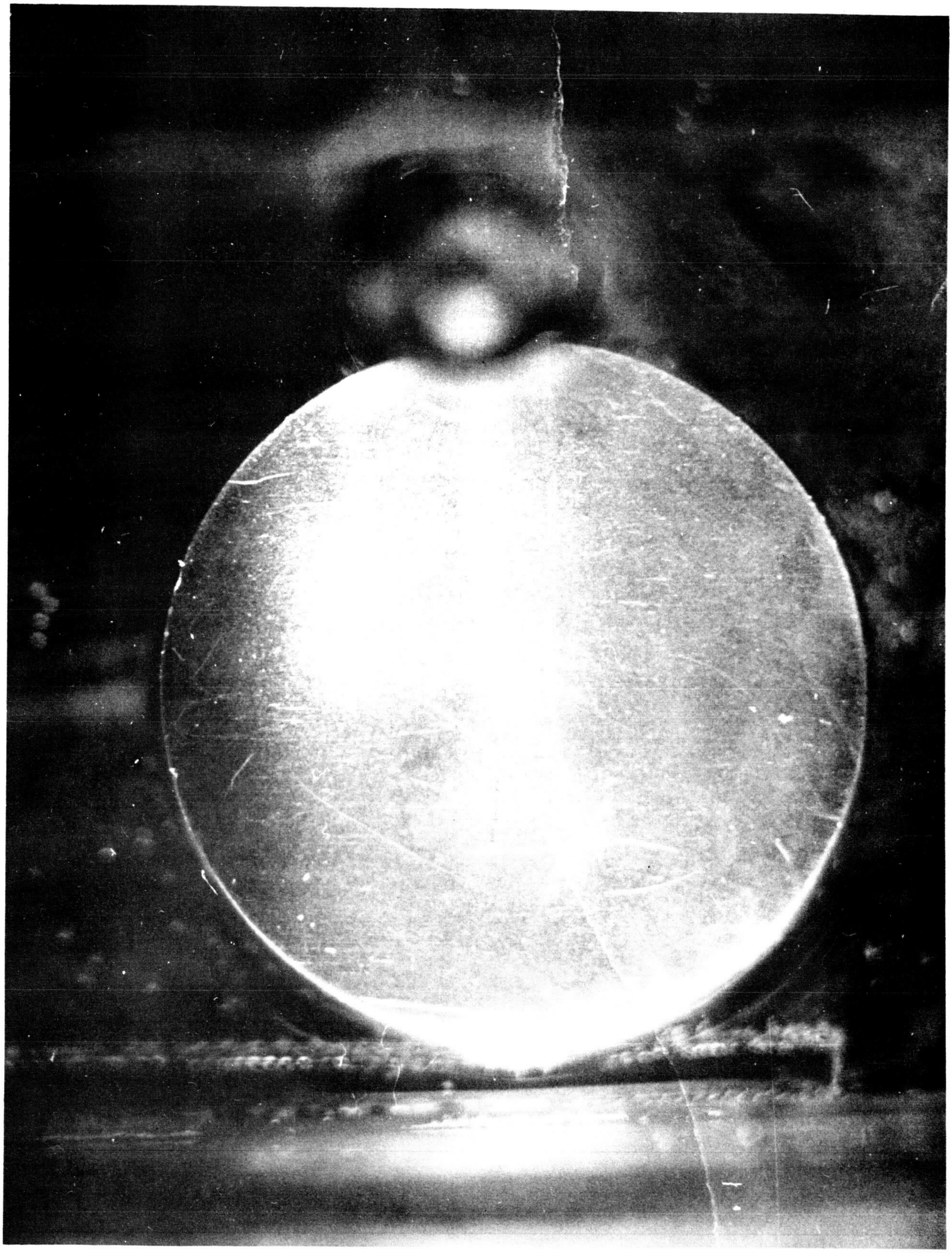
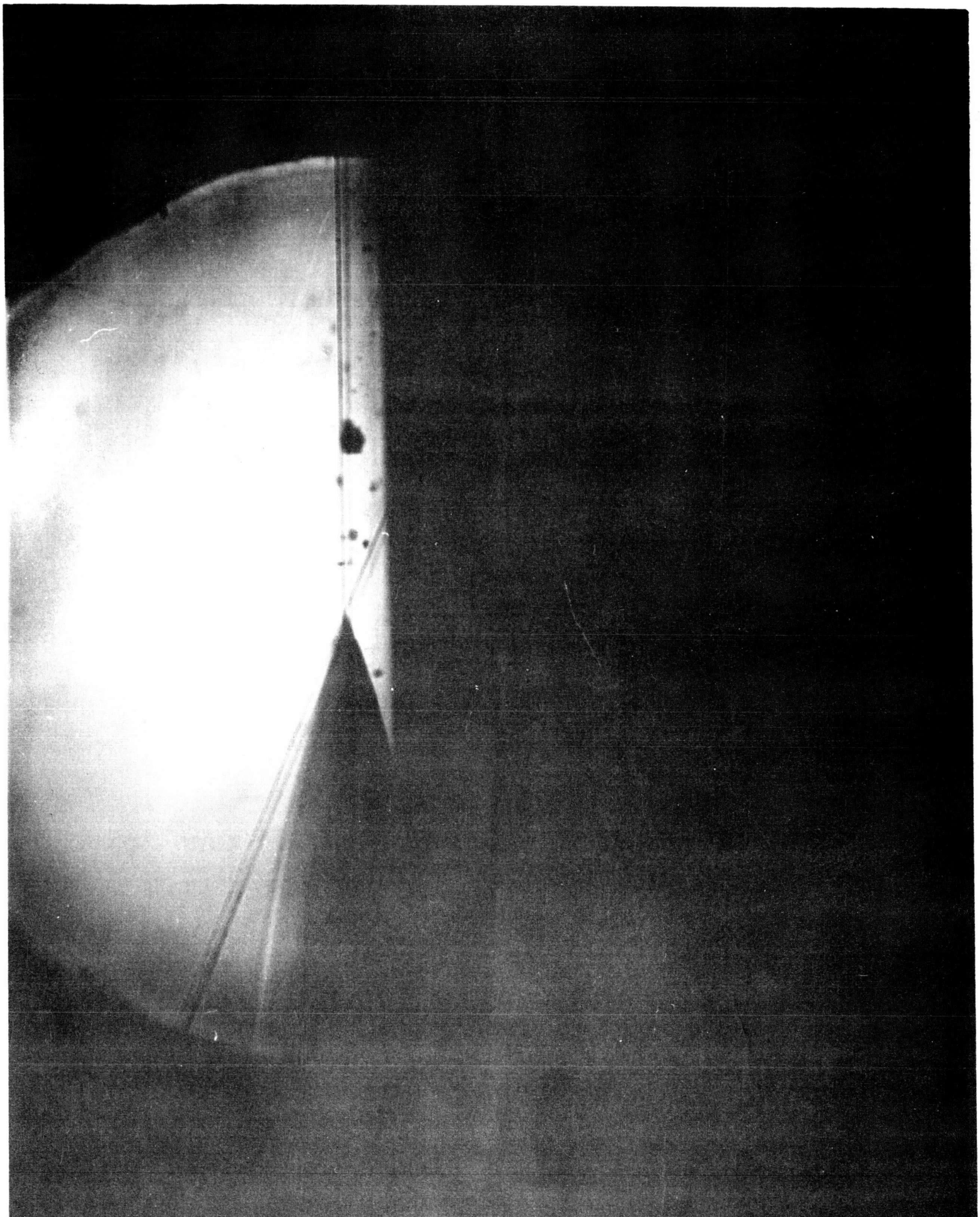


Figure 3

The Profile of a Drop of 90% Hydrogen Peroxide on Polished Aluminum



measurement of the surface tension of hydrogen peroxide since platinum is a specific decomposition catalyst for hydrogen peroxide. The accuracy of this method was confirmed by measuring the surface tension of conductivity water which was 72.71 dynes cm^{-1}. The literature value (averaged) for the surface tension of water (12) was 72.75 dynes cm^{-1}, and a calculated value (13) was 72.80 dynes cm^{-1}.

3. Density Measurements

The procedure used to measure the densities of the liquid propellants was a modified Westphal method described by Steinbach and King (14). Briefly, the method consisted of weighing a submersible body in air and then immersed in the test liquid. A calibration of the submersible body was obtained by using water as one of the test liquids. A near isothermal measurement was achieved by placing the test liquid in a jacketed cell through which constant temperature water was circulated. A modified analytical balance was used to obtain the weights.

Details of a modified Westphal method for measuring the density of hydrogen peroxide solutions in water have been presented by Wynne Jones et al (16).

4. Cleaning and Handling Techniques

Cleaning reagents -- Analyzed ACS Grade reagents were used for the sulfuric-nitric acid and alcohol KOH cleaning solutions. Commercial "Tide" was used for planchet washing. Conductivity water brought to the boil in an all glass Pyrex wash-bottle was used for routine rinsing.

Handling Techniques

Optical cell cleaning -- The optical cell used for contact angle measurements was cleaned routinely by filling the cell with a saturated solution of KOH in isopropanol and allowing the cell to stand for at least 1 hour. After emptying the cell, the residual base was extracted exhaustively (at least 10 times) with boiling conductivity water. The test for cell cleanliness was the complete wetting (absence of "water break") of the cell surfaces by room temperature conductivity water. The cell cover was cleaned by immersion in hot mixed nitric and sulfuric acids (2:1 vol. ratio respectively) and rinsed with boiling conductivity water.

When measurements were to be made with liquids other than conductivity water, the residual water was extracted with the test liquid.

Glass pipette cleaning -- Capillary glass pipettes were stored in mixed nitric-sulfuric acids (17) at room temperature immediately after drawing. No pipette was used unless it had stood in the mixed acids for at least 24 hours. Each pipette used was drained of acid, rinsed exhaustively (at least 10 times) with boiling conductivity water, and dried by extraction with absolute ethanol and flamed. The clean, dry pipette was then placed through the cover plate hole and kept there for the duration of a measurement.

Solid specimen cleaning -- Polished or satinized metal specimens were washed with Tide (18) and running hot tap water using a camel's hair brush. A final Tide wash and rinse was done with boiling conductivity water. The residual water film was allowed to flash off the hot specimen, which was then placed in the contact angle cell.

Glass specimens (17) were stored in mixed nitric-sulfuric acid at room temperature. For use, they were rinsed with boiling conductivity water, then heated by placing them in a container of boiling conductivity water. The glass specimens were withdrawn from the boiling conductivity water under continuous flushing with boiling conductivity water. This technique insured the rapid flash of residual water from the glass specimen.

Stainless steel tongs -- The stainless steel tongs used for handling the solid specimens were swirled in hot mixed nitric-sulfuric acids and rinsed with boiling conductivity water prior to use.

Specific gravity cell -- The cylindrical, jacketed specific gravity cell was cleaned with alcoholic KOH as described for the contact angle cell. A Plexiglass cover was cleaned with hot Tide solution, rinsed with boiling conductivity water, and the residual water extracted with the test liquid. This cell was also used for the surface tension measurements.

Westphal bob -- The Westphal bob was stored in mixed nitric-sulfuric acids, rinsed with boiling conductivity water, and air dried for use.

Glass hanger -- The glass hanger used for the density measurement on the 90% hydrogen peroxide was stored in mixed nitric-sulfuric acids, rinsed with boiling conductivity water, and air dried for use.

RESULTS AND DISCUSSION

The experimentally determined results are presented and discussed in detail in the following sub-sections. The highlights of the results of the contact angle studies are as follows: Initially, all the liquids spread spontaneously with advancing contact angles of 2° or less on all the solid (Table II) surfaces. However, a large increase in the advancing contact angle (up to 30°) occurred on polished aluminum aged for thirty minutes using drops of both water and 90% hydrogen peroxide. The surface of polished type 301 stainless steel also became hydrophobic when aged in the presence of water vapor.

TABLE II

DENSITIES AND SURFACE TENSIONS OF LIQUID PROPELLANTS AND WATER

Liquid	Density ($g\ cc^{-1}$) 20°C.		Surface Tension ($dynes\ cm^{-1}$) 20°C.	
	Found	Lit.	Found	Lit.
Water	0.9979	0.9982(15)	72.5	72.75(12)
Absolute ethanol	0.7888	0.7893(21)	22.4	22.75(22)
Hydrazine	1.004	1.002@25°/4°(23)	63.2	66.67(23)
UDMH (uns-dimethyl hydrazine)	0.7895	0.7845@25°/4°(24)	24.4	28@25°(24)
Arizine 50-(0.5/0.5)N_2H_4/UDMH	0.8891	--	30.3	--
Fuming nitric acid Type IIIB	1.556	1.560(25)	44.0	--
di-Nitrogen tetroxide	1.4595@15°/4°	1.4470(26)	27.0	--
Hydrogen peroxide 90%	1.3931	1.3915(27)	79.09(*)	79.15(27)

The measurement temperature for all the liquids except nitrogen tetroxide was 20.00±0.05°C. The measurement temperature for the nitrogen tetroxide was 14.00°±0.05°C.

The sensitivity of the analytical balance was ±0.5 mg. when the bob was immersed in the liquid.

The surface tensions of all the liquids except the 90% hydrogen peroxide were measured with the duNouy tensiometer. The surface tension of the 90% hydrogen peroxide was measured with the glass Wilhelmy plate.

Unusual effects were observed with many of the liquid solid combinations in which a drop of liquid was observed to retain its configuration while resting on a thin layer of its own liquid. One would normally expcet a wetting liquid to spread into a thin flat sheet on the solid surface as alcohol does. Interference colors were observed to exist for short periods of time on the solid surface surrounding the drop, which confirmed the presence of a thin liquid layer extending outward from it. From these observations, the conclusion was drawn that, regardless of the mechanism that caused the drop to remain discreet, true wetting of the solid surface by the liquid had occurred. It is believed that these drops are a manifestation of the wineglass effect. This effect is due to surface tension gradients generated by unequal evaporation rates of the components of mixtures of liquids having different surface tensions. Surface tension gradient effects have been described for alcohol-water systems by Thompson (19) and more recently by Bascom et al (20) for the spreading of oils on solid surfaces.

From the low values of the measured contact angles and from the observations of the spreading effects of the liquid propellants on the solid surfaces, the liquid propellants were said to wet the surfaces of the tank materials with a true zero contact angle. The term wetting is used in a very restrictive sense in this report to mean initial spontaneous spreading with a corresponding near zero contact angle.

Densities and Surface Tensions of Liquid Propellants

Table II presents the experimentally determined density and surface tension values for the liquid propellants together with comparison values taken from the literature. The data for water are presented first since these measurements gave a verification of the experimental procedures and provided a calibration of the Westphal bob for the density determinations of the remaining liquids. The data for the four fuels are presented next as a group followed by the data for the three oxidizers. This order was chosen since the experimental procedures for the density and surface tension measurements on the 90% hydrogen peroxide were different from those used for the other liquids.

The data for absolute ethanol were in fair agreement with literature values (21, 22)

Baker and Gilbert (23) measured the surface tension of aqueous hydrazine solutions using the maximum bubble pressure method with hydrogen instead of air as the bubble forming gas. According to their results, the surface tension of hydrazine measured in an air atomsphere was lower than that measured in a hydrogen atmosphere. The surface tension value of hydrazine in the present work measured in an air atmosphere saturated with hydrazine vapor is consistent with Baker and Gilbert's observation.

The literature value for the surface tension of UDMH (24) is substantially higher than was found in the present work. No literature references were found for either density or surface tension values of the Arizine 50 blend.

A comparison value for the density of the nitric acid was derived from data supplied by the manufacturer (25). A recorded value of 1.560 g cc^{-1} was found to correspond to the analysis of the nitric acid sample. The experimentally determined value from the present work was 1.556 g cc^{-1}, in fair agreement with the recorded value. The lower measured value was probably due to loss of NO_2 during handling. Although no comparison values for the surface tension of the nitric acid were found, an interpolation of data for 99.8% nitric acid gave a value of γ = 40 dynes cm^{-1} (approx) at 20°C. The experimentally determined surface tension value for the nitric acid of γ = 44.0 dynes cm^{-1} at 20°C. is probably in the correct range for this material, assuming that the dissolved HF stabilizer raises the surface tension.

A comparison value for the density of nitrogen tetroxide was supplied by the manufacturer (26). No value for the surface tension of this material was found in the literature.

Comparison values for both the density and surface tension of the 90% hydrogen peroxide were obtained from a linear interpolation of data quoted by the manufacturer (27). The experimentally determined values were in fair agreement with the derived comparison values.

The largest known deviation in the measured densities was 0.3%, for the density of the nitric acid.

Initial Contact Angles of the Liquid Propellants on Freshly Cleaned Solid Surfaces

Table II presents the initial advancing and receding contact angle data observed for each of the liquid propellants on each of the solid substrates. Drops of all the liquids except water and 90% hydrogen peroxide continued to spread after the initial drop was placed on the solid surface. The contact angles of these spreading drops were not static equilibrium contact angles but rather were the measured angle of a moving front of liquid which was in equilibrium with an air atmosphere nearly saturated with the liquid vapor. Withdrawing an increment of liquid from these spreading drops momentarily stopped the spreading, and the resulting observed angle was recorded as the receding angle. As used in this report, a zero degree contact angle means that the liquid has spread in a thin flat sheet and the observed liquid-solid-vapor interfacial angle is less than 0.5 degree.

Drops of water and hydrogen peroxide did not continue to spread on the solid surfaces but assumed a stationary position after the initial advance of the drop. The contact angles reported are the contact angles of this stationary position. Some contact angle hysteresis was observed when increments of liquid were withdrawn from drops of water or 90% hydrogen peroxide to form receding angles. The observed hysteresis effect was that the planchet area, covered by the drop when the liquid advanced, remained covered by liquid when the increment was withdrawn. From the observations that the resulting drop had a lowered height, volume, and contact angle, the conclusion was drawn that the solid-liquid interfacial area had not changed appreciably. Visual inspection of the drop showed that the drop solid-liquid interfacial perimeter apparently had not contracted when liquid was withdrawn from the drop. Since the receding angle could be made to vary from the value of the advancing angle to zero simply by removing liquid from the drop, an arbitrary receding angle was generated by removing from the drop nearly the same volume of liquid which had been previously added to the drop to generate the advancing angle. By using initial liquid drops of approximately 1 mm in diameter, then adding an increment of liquid to generate the advancing angle, then withdrawing an equal increment to generate the receding angle, variations in the contact angle due to initial drop size and liquid increment size were minimized. Reproducible values for the receding angles were obtained in this way. This hysteresis effect implies that once the finite energy barriers to spreading have been overcome by the work input to the liquid, the surface remains wettable by the liquid. These energy barriers may be due to weakly adsorbed contaminants, random roughness of the polished surface, or transitions and hydration in the metal oxide surface structure.

The Effect of Surface Aging on the Contact Angle

The liquids which showed a change in the observed contact angles with surface aging were water and 90% hydrogen peroxide. Figures 4 and 5 compare the observed contact angles with aging times up to 30 minutes for water on polished and satinized metal surfaces. Figure 4.4 gives the same comparison for water on Pyrex glass. Similar comparisons are shown for 90% hydrogen peroxide on polished metal surfaces, Pyrex glass, and satinized metal surfaces in Figures 6 and 7 respectively.

The advancing contact angle of water on polished aluminum increased from 3° to about 30° over the 30 minute time period (Figure 4.1). These observations probably reflect the gradual formation of a hydrophobic layer on the surface of the aluminum as it aged. The formation of such a layer was probably due to adsorption of organic vapors from the atmosphere. This was clearly demonstrated by White (30) who showed that aluminum exposed only to pyrolyzed air remained hydrophilic and water wettable. The pyrolysis evidently removed the organic contaminants from the air. When the same sample of aluminum was exposed to unpyrolyzed air, the surface became hydrophobic in a few minutes just as it did in the present work.

Figure 4

Water on Polished Solid Surfaces

Figure 4.1. 6061 T6 Aluminum

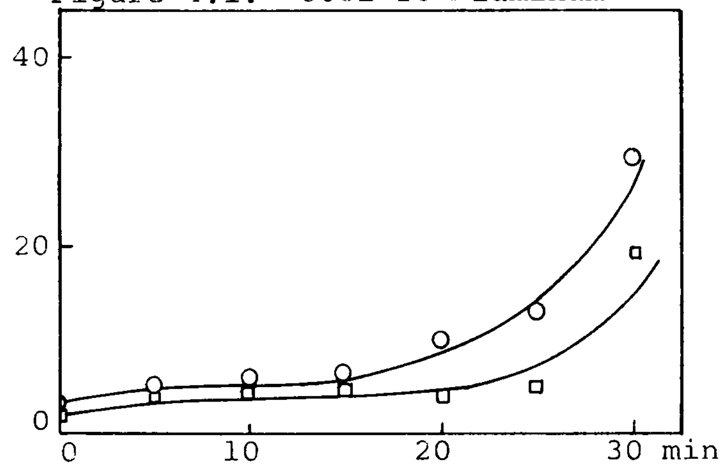


Figure 4.2. Grade 6 Titanium Alloy

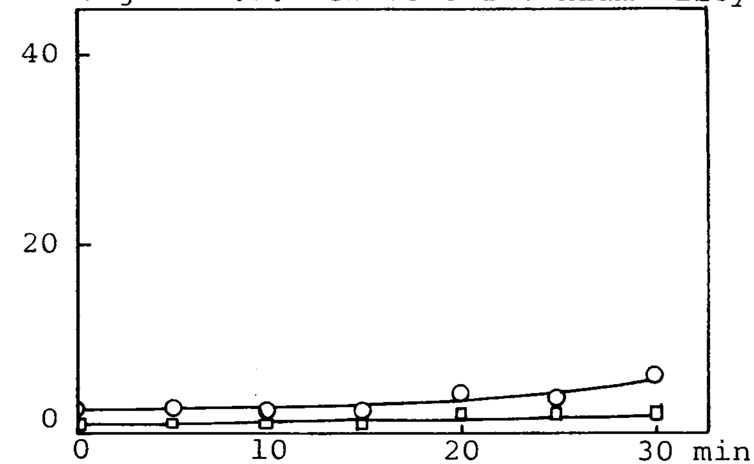


Figure 4.3. Type 301 Stainless Steel

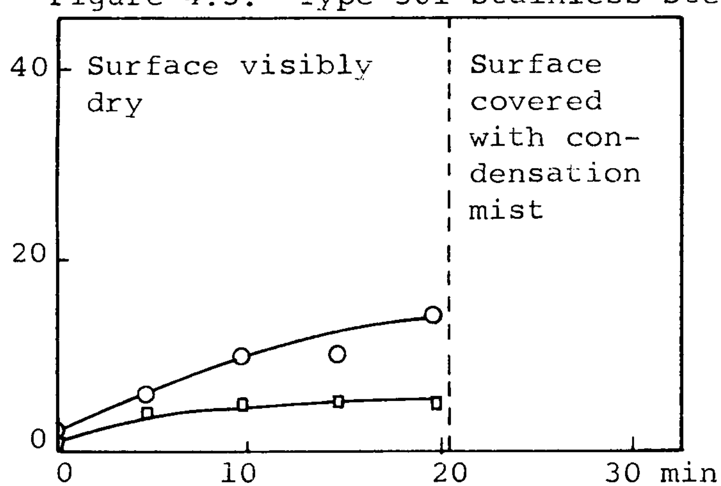
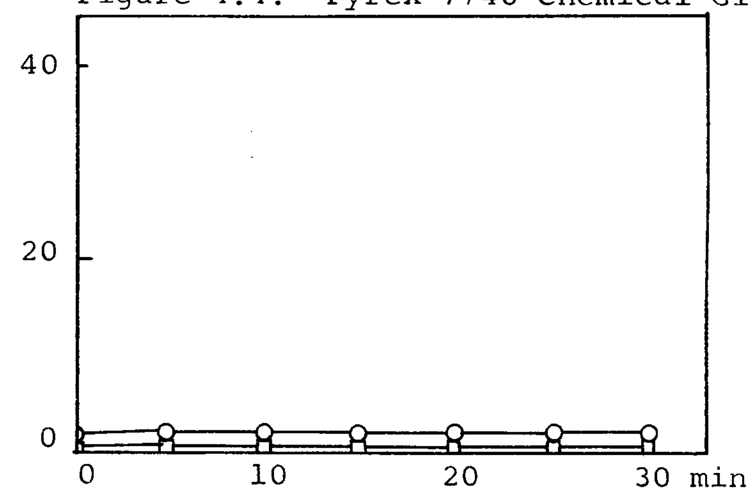


Figure 4.4. Pyrex 7740 Chemical Glass



○ = Advancing angle

□ = Receding angle

Figure 5

Water on Satinized Metal Surfaces

Figure 5.1. 6061 T6 Aluminum

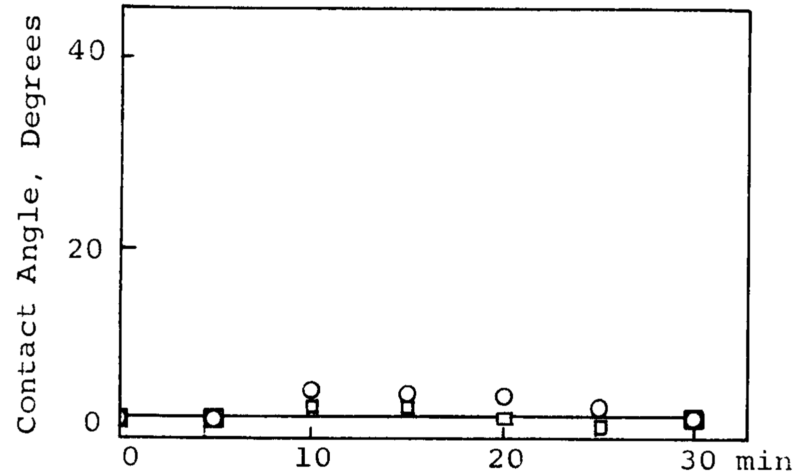


Figure 5.2. Grade 6 Titanium Alloy

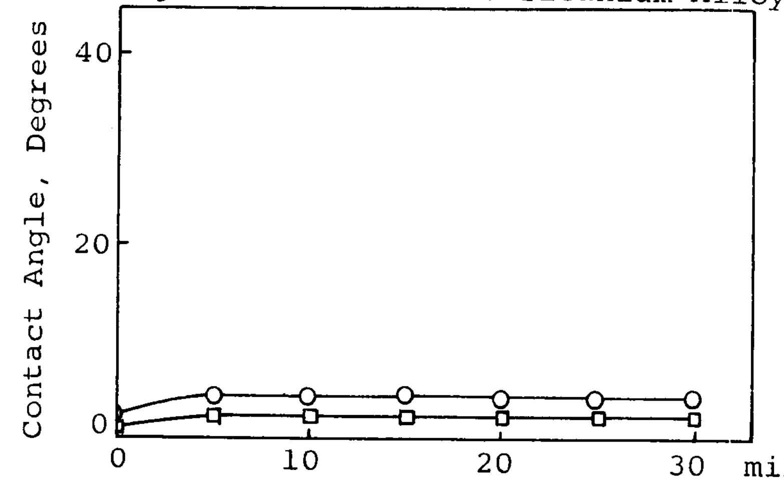
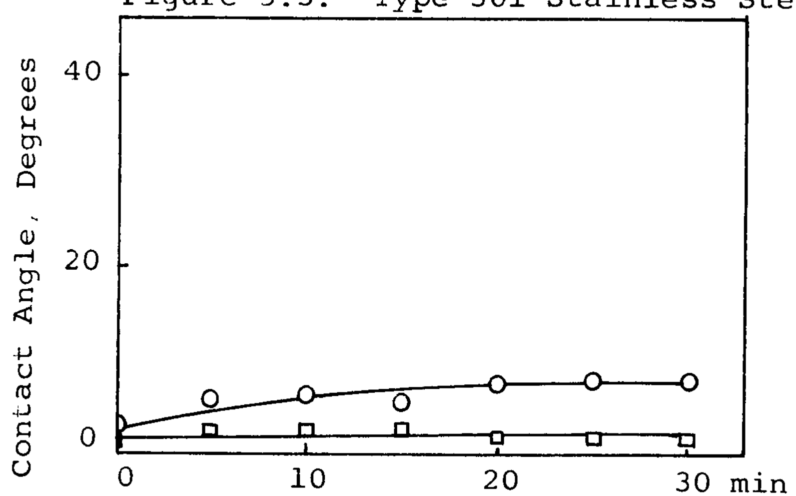


Figure 5.3. Type 301 Stainless Steel



o = Advancing

□ = Receding

Figure 6

90% Hydrogen Peroxide on Polished Solid Surfaces

Figure 6.1. 6061 T6 Aluminum

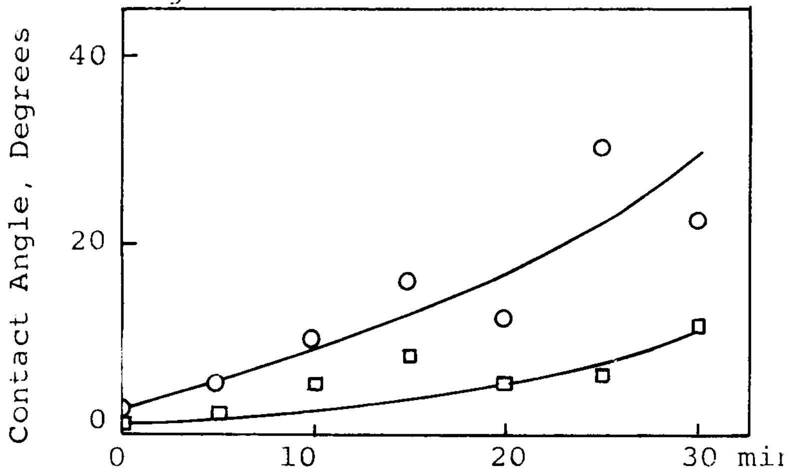


Figure 6.2. Grade 6 Titanium Alloy

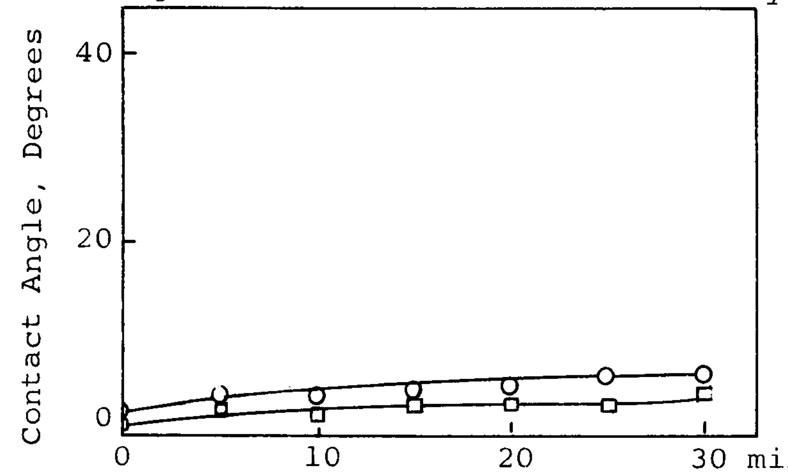


Figure 6.3. Type 301 Stainless Steel

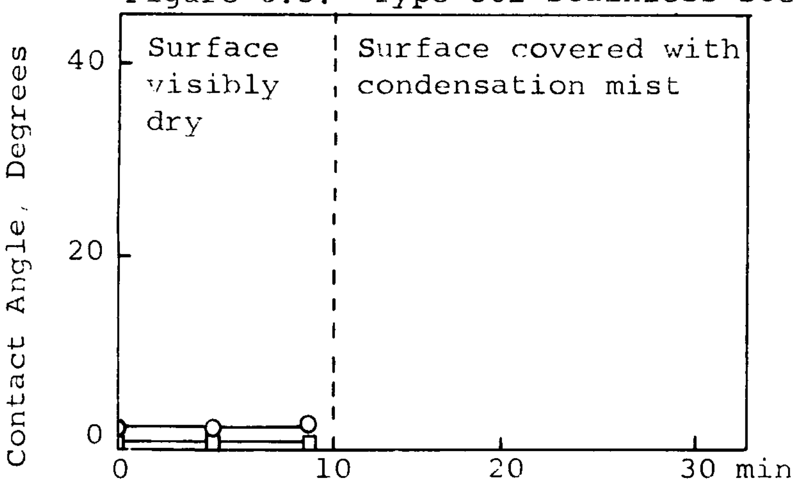
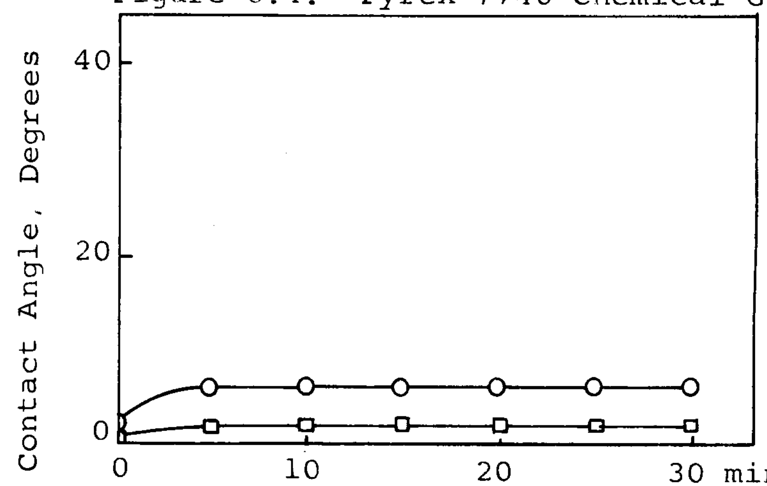


Figure 6.4. Pyrex 7740 Chemical Glass



○ = Advancing

□ = Receding

Figure 7

90% Hydrogen Peroxide on Satinized Metal Surfaces

Figure 7.1. 6061 T6 Aluminum

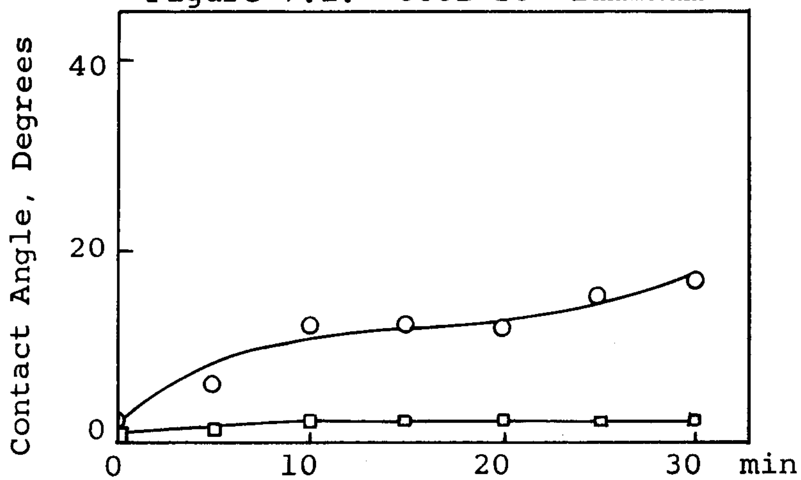


Figure 7.2. Grade 6 Titanium Alloy

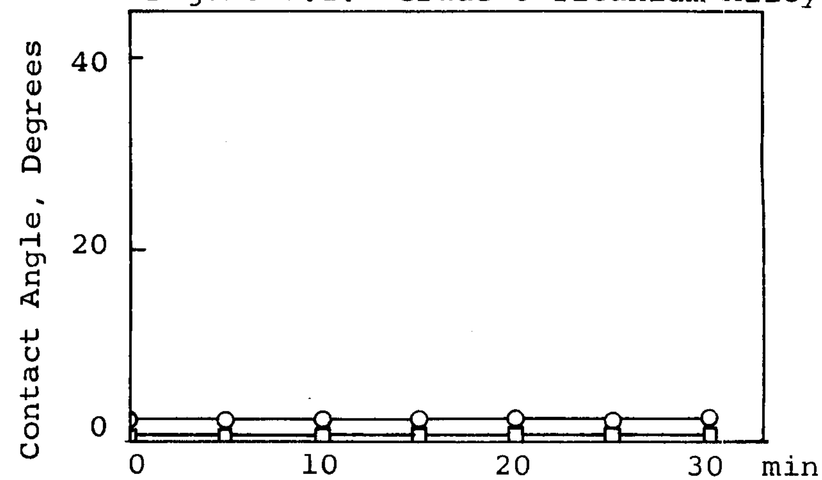
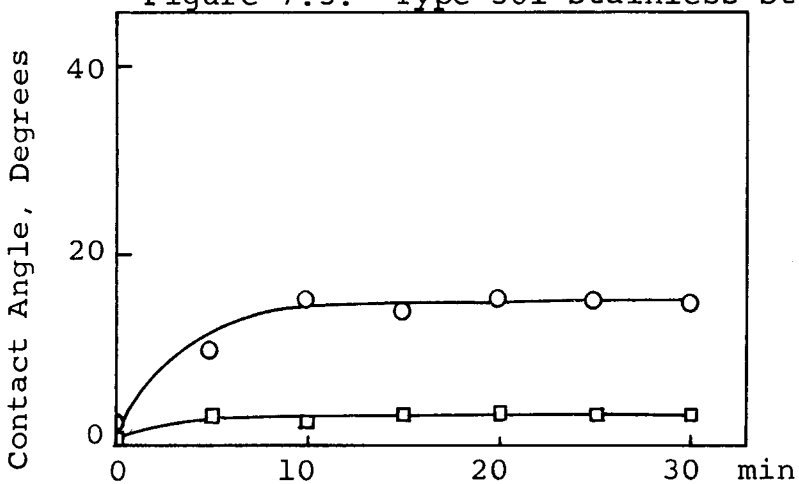


Figure 7.3. Type 301 Stainless Steel



○ = Advancing

□ = Receding

The advancing contact angle of water on polished stainless steel increased from 2° to 14° in 20 minutes on a visibly dry planchet surface. After 20 minutes, condensation on the planchet surface caused coalescing of the test drop with minute droplets beyond the test drop boundary resulting in an artifically low contact angle.

The effect of satinizing the planchets was to keep the liquid-solid contact angle low under the same aging conditions that produced a hydrophobic surface on the polished planchets (Figure 5). Pyrex 7740 chemical glass remained hydrophilic during aging (Figure 4.4).

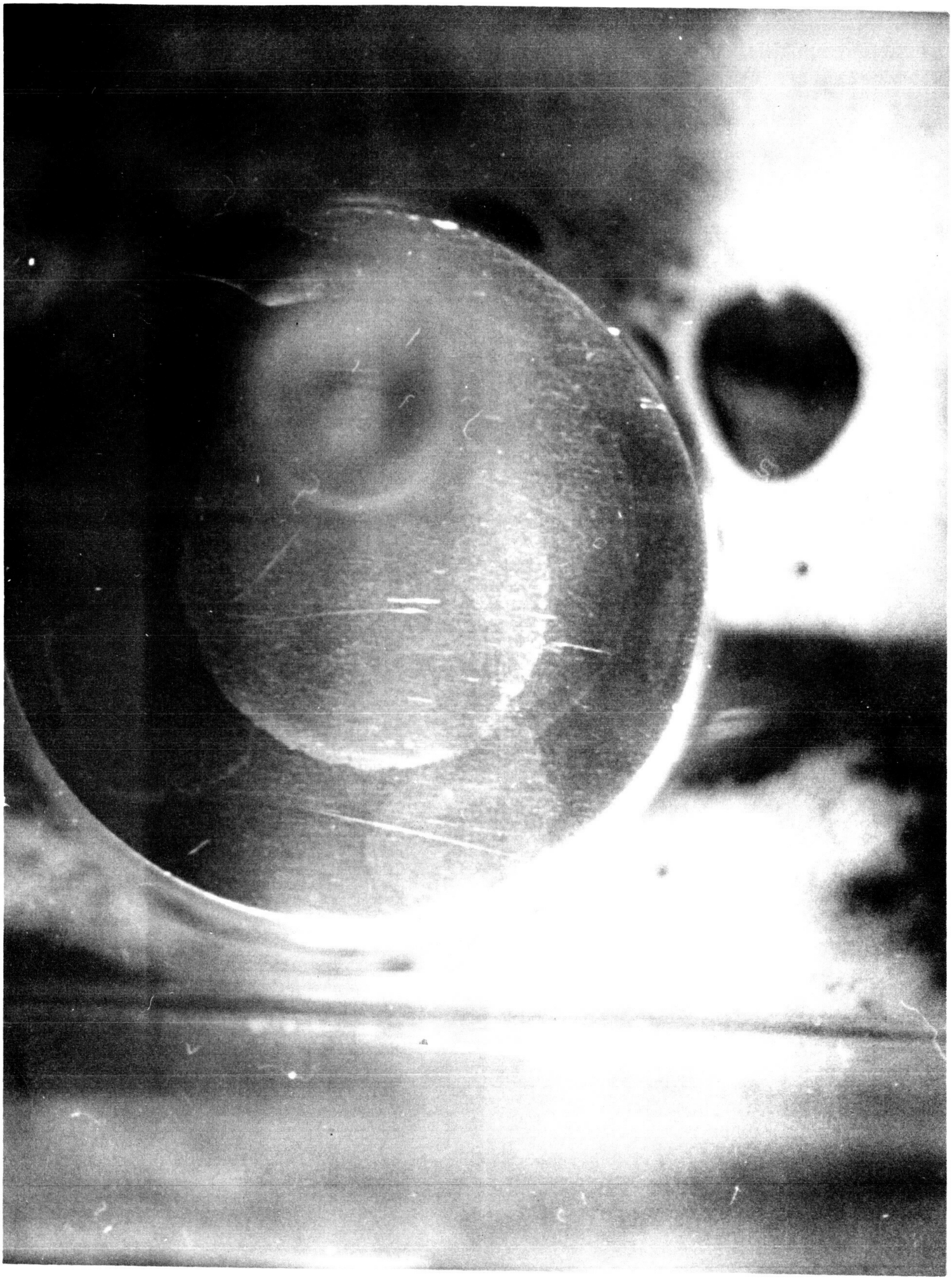
Several effects were shown by the 90% hydrogen peroxide on the solid surfaces. Polished aluminum (Figure 7.1) became hydrophobic during the 30 minute aging period, this behavior is similar to that obtained with water. The polished Type 301 stainless steel remained wettable by the 90% hydrogen peroxide during the aging period while the polished titanium alloy (Figure 7.2) and Pyrex 7740 chemical glass (Figure 8) slowly developed a hydrophobic surface.

Apparent large contact angles were observed for drops of 90% hydrogen peroxide on satinized aluminum and Type 301 stainless steel. When these drops were viewed from above, a wet area could be seen extending outward from the perimeter of the liquid-solid interfacial boundary indicating that liquid had migrated from beneath the drop out along the surface of the roughened planchet. From the fact that this extra-peripheral liquid remained in a thin flat sheet, the conclusion was drawn that the roughened surface was being wet by the 90% hydrogen peroxide with an accompanying zero true contact angle. The drops with the apparent large contact angle were probably in metastable equilibrium. Although the parameters which control these anamalous drops were not clearly separated in this work, wicking of the liquid along a roughened surface was probably an important parameter. This behavior of liquid remaining as a discreet drop upon a wet surface was observed for many of the liquid-solid combinations. These spreading effects are discussed in the next section.

Marangoni Effect

The Marangoni or "wineglass" effect consists of a heaving or bulging in a liquid surface due to mass transport along the surface caused by surface tension gradients. This phenomenon occurred with several of the liquids in this study, namely, UDMH, Arizine 50 blend, nitric acid propellant Type IIIB, and di-nitrogen tetroxide. When the phenomenon occurred it gave a false appearance of a drop of liquid forming an appreciable contact angle. Close examination of the system showed the presence of a thin liquid film extending from the periphery of the drop out over the surface of the planchet.

Figure 8
A Drop of Absolute Ethanol Viewed From Above Spreading on Polished Aluminum
With a Near-Zero Contact Angle



Bascom and Singleterry (21) have demonstrated that a mixture of liquids of different evaporation rates and surface tensions is a requirement for this effect. The different evaporation rates lead to localized differences in concentration of the two liquids which in turn lead to areas of the liquid having different surface tensions. Due to the tendency of a system to minimize its surface energy, the areas of low surface tension spread toward the high ones dragging underlying liquid along. This produces a pile up of liquid which gives the appearance of a drop or non-wetting system. This appearance of non-wetting is, however, an illusion. The liquid actually wets the solid.

All of the liquids which exhibited this effect must be mixtures. In fact, they are all mixtures, either as originally prepared as in the case of nitric acid or become mixtures due to decomposition as in the case of N_2O_4 and 90% hydrogen peroxide.

The appearance of a Marangoni effect drop in contrast with a drop forming a finite contact angle may be seen by comparing Figure 8 with Figure 9.

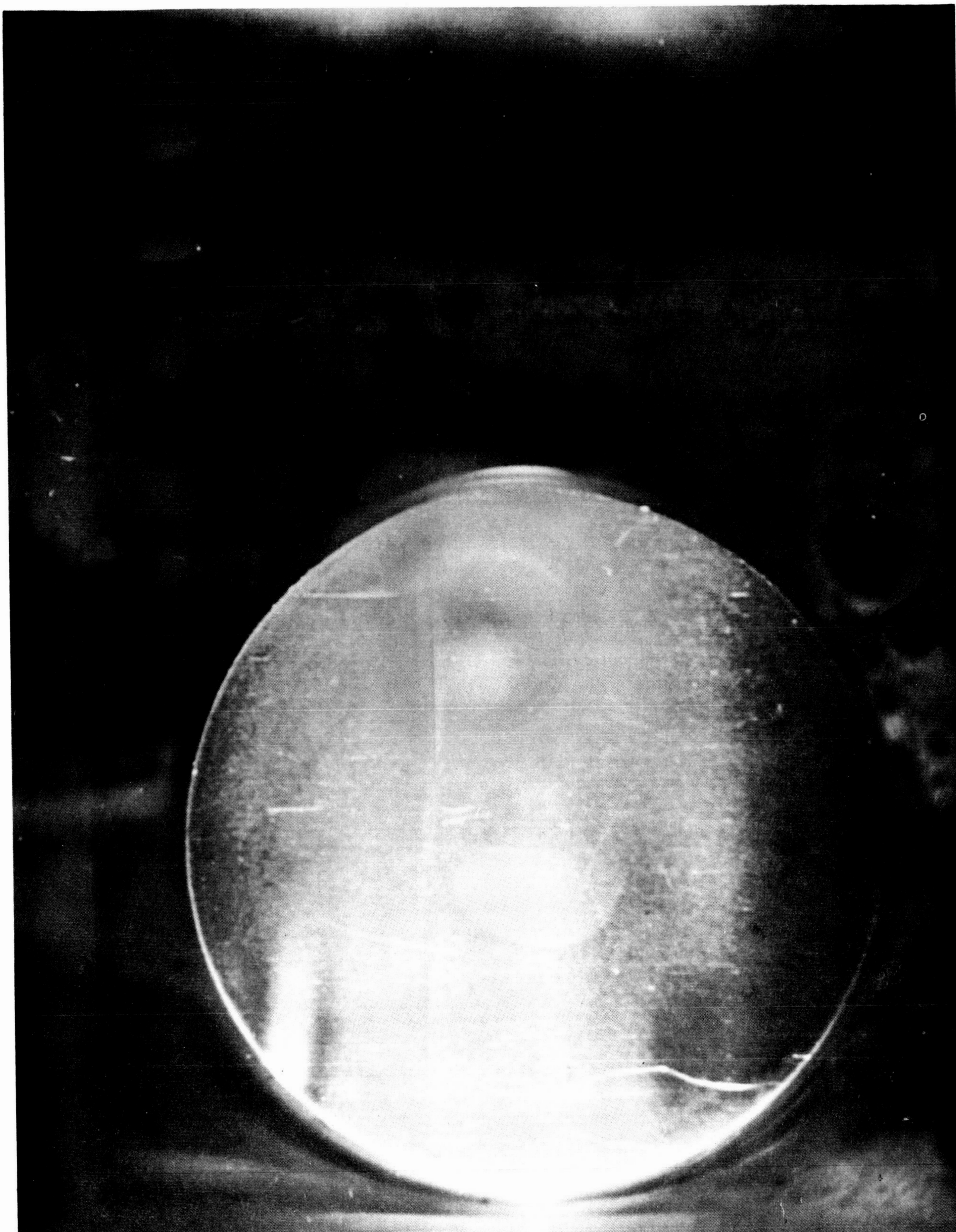
CONCLUSIONS

1. All of the liquids spread on all of the freshly cleaned solids to a near zero contact angle.

2. Polished aluminum and 301 stainless steel become hydrophobic a few minutes after cleaning so that water and 90% hydrogen peroxide form substantial contact angles on their surfaces.

Figure 9

A Drop of UDMH Viewed From Above Showing the Interference Bands (arrow) During the Operation of the "Wineglass Effect"



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